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**Title:** Shale gas and non-aqueous fracturing fluids: opportunities and challenges for supercritical $CO_2$

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# Shale gas and non-aqueous fracturing fluids: opportunities and challenges for supercritical $CO_2$

## Abstract

Hydraulic fracturing of shale formations in the United States has led to a domestic energy boom. Currently, water is the only fracturing fluid regularly used in commercial shale oil and gas production. Industry and researchers are interested in non-aqueous working fluids due to their potential to increase production, reduce water requirements, and to minimize environmental impacts. Using a combination of new experimental and modeling data at multiple scales, we analyze the benefits and drawbacks of using $CO_2$ as a working fluid for shale gas production. We theorize and outline potential advantages of $CO_2$ including enhanced fracturing and fracture propagation, reduction of flow-blocking mechanisms, increased desorption of methane adsorbed in organic-rich parts of the shale, and a reduction or elimination of the deep re-injection of flow-back water that has been linked to induced seismicity and other environmental concerns. We also examine likely disadvantages including costs and safety issues associated with handling large volumes of supercritical $CO_2$. The advantages could have a significant impact over time leading to substantially increased gas production. In addition, if $CO_2$ proves to be an effective fracturing fluid, then shale gas formations could become a major utilization option for carbon sequestration.

## Keywords

Shale gas; hydraulic fracturing; supercritical $CO_2$; non-aqueous fracturing fluids; waterless fracturing fluids.

## 1 Introduction

Hydraulic fracturing has substantially increased shale oil and gas production, helping generate a domestic energy boom and lower hydrocarbon costs in recent years. The tight shale formations where this oil and gas are stored have permeabilities that are typically in the nanodarcy range ($10^{-21}$ $m^2$) and that prohibit efficient extraction using conventional methods. Hydraulic fracturing, the process of injecting a fluid—typically water—into a target formation at pressures high enough to fracture the rock, is performed to increase permeability and thereby increase production. Figure 1 provides a caricature of hydraulic fracturing, including highlighting where the gas is extracted from in the shale formation. The length scales involved in shale gas production cover thirteen orders of magnitude, ranging from nanometer size pores where methane is trapped, and sometimes up to kilometer long fractures that are conduits to the production well [1]. Interest in the use of hydraulic fracturing for increased production, and the use of shale gas as an alternative fuel, is drawing attention around the world [2-12].

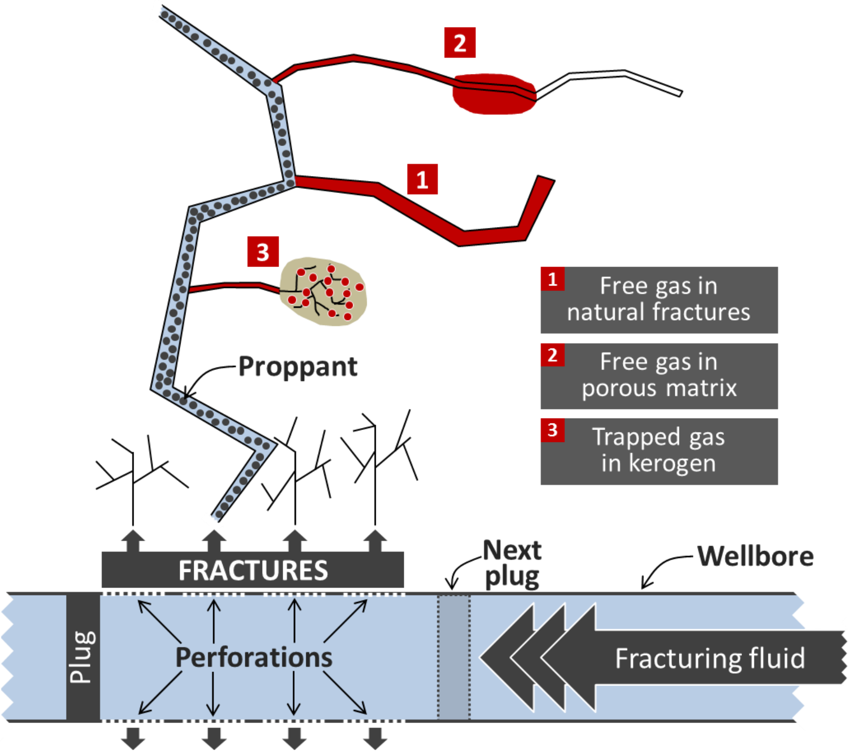

*Figure 1: Schematic of a fracturing system highlighting induced and natural fractures and three primary gas-in-place origins of methane. An alternative fracturing fluid such as $CO_2$ may more efficiently extract gas from (1) and (2) since $CO_2$ is miscible with hydrocarbon thereby preventing multi-phase flow blocking and from (3) since $CO_2$ can exchange with methane that is sorbed to kerogen.*

Presently, water is the only fracturing fluid regularly used in commercial shale gas and shale oil production due to its low cost, ready availability, and its suitability for fracturing. The recent rapid oil and gas production expansion, though, has led to water use issues. For example, states such as Texas, North Dakota, Kansas, Colorado and Pennsylvania have encountered water-availability issues related to drought that have impacted fracturing, including the denial of drilling permits [13]. A typical shale gas well injects between 2 and 4 million gallons of water into a deep shale reservoir [14, 15]. Between 15 to 80% of this water (known as flow-back water) is recovered in the early stages of gas production depending on geology and other factors [16, 17]. Flow-back water and produced water (i.e., water present in the shale formation that is produced along with the hydrocarbon) is contaminated with secondary substances that are added to the water to enhance fracture generation, such as hydrochloric or muriatic acid during the acid stage (e.g., dissolves carbonate minerals and opens fractures near the wellbore), gelling agents (e.g., to increase amount of propping agents the fluid can carry), and chemical modifiers (e.g., bactericides, corrosion inhibitors, and friction reducers), along with other substances (e.g., metals, radionuclides) from the hydrocarbon reservoir [18, 19]. Consequently, this flow-back water has to be treated and/or disposed of, usually through deep re-injection into geologic formations that do not interfere with the fracturing site or transportation to water-treatment facilities or other fracturing sites. Large-scale water disposal via deep re-injection has been linked to triggered seismicity that results in low-level earthquakes [20, 21]; using non-aqueous fluids would likely reduce the need for large volumes of water re-injection. Furthermore, hydraulic fracturing has also been associated with potential freshwater contamination during the injection/production phases as well as with water disposal [16, 22-24]. For these reasons reducing the use of water in hydraulic fracturing is a high priority for industry, policy makers, and concerned environmental groups. Reducing or eliminating water requirements could, for example, play a key role in the United States' attempts to minimize pressure on the energy-water nexus without negatively impacting energy production growth. This possible reduction has stimulated the exploration into the use of non-aqueous fracturing fluids (e.g., hydrocarbons and supercritical $CO_2$ [25]) and non-fluid fracturing (e.g., explosives-based [26-28]) approaches.

Supercritical $CO_2$ is a notable non-aqueous fracturing fluid currently under consideration for use in hydraulic fracturing. $CO_2$ is part of a class of energized fluids or foams that have been gaining interest, particularly as the limitations with conventional fracturing fluids becomes more apparent [29, 30]. For example, energized fluids (fracturing solutions that contain inert gases) account for fracturing in around 40% of horizontal wells in Canada, though only around 2% in the United States [31].Super critical $CO_2$ offers several significant advantages over water, as well as some potential drawbacks. Key potential advantages for $CO_2$ include increased methane ($CH_4$) and hydrocarbon production due to miscibility with hydrocarbons, enhanced fracturing properties, reduced pressurization requirements at the well pad (i.e., depending on formation depth, the $CO_2$ arriving at pipeline pressure may require little or no further pressurization) , effective gas displacement from fractures with poor connectivity, enhanced desorption of $CH_4$ from organics present in the shale, and the reduction/elimination of injection and flow-back water. In addition, if $CO_2$ is an effective fracturing fluid, then shale gas formations could become a major utilization option for the Department of Energy's Carbon Capture, Utilization, and Storage program providing that one can demonstrate that $CO_2$ can be safely stored in these formations. Although injectable $CO_2$ is currently a scarce resource national sequestration targets, which could involve capturing $CO_2$ from hundreds of fossil-based power plants [32], would lead to a need to store large volumes of $CO_2$ away from the atmosphere. In turn, this could result in large volumes of $CO_2$ being used for shale gas production, a significant reduction of water usage for fracturing, and large-scale storage of $CO_2$. Potential drawbacks, however, include the increased expense of capturing-pressurizing-transporting $CO_2$, robust accounting of $CO_2$ emissions and storage, pressure safety at the site, separation of hydrocarbons and brine from the flow-back $CO_2$, and re-pressurization of flow-back $CO_2$.

The overall economic comparison between water and $CO_2$ (or any alternative working fluid) depends primarily on its influence on gas production effectiveness (i.e., if $CO_2$ as a fracturing fluid does not produce more hydrocarbons than water, then it will never justify its increased cost) as well as additional costs associated with environmental impacts, the economics of $CO_2$ delivery, and flow-back $CO_2$ treatment cost. It is unlikely that industry will switch to non-aqueous working fluids unless there is a demonstrable and reliable increase in production that justifies the increased costs of alternative fracturing methods. Commercial enhanced oil recovery (EOR) operations currently being investigated under the DOE Regional Carbon Storage partnerships program have shown promise that EOR can be carbon neutral. For example, the Southwest Partnership is studying an EOR site in the Farnsworth formation where $CO_2$ is being used to extract oil with $CO_2$ being sequestered in the process [33]. Shale gas could be another utilization possibility for $CO_2$, but the feasibility of this option needs to be further investigated.

This paper addresses the potential effectiveness of using $CO_2$ as alternative working fluid for shale gas production, including an extensive literature review regarding conventional and non-conventional shale gas fracturing. Using a combination of theory, new experimental data, and new modeling data, we discuss and demonstrate how $CO_2$ could significantly increase shale gas production. Specifically, $CO_2$ could expand production through enhanced fracturing and fracture propagation, reduced flow blocking by the working fluid ($CO_2$ is miscible with the produced hydrocarbons), and increased desorption of methane adsorbed in organic-rich parts of the shale [34, 35]. In addition, pores can be become blocked using aqueous fracturing fluids, due clay mineral swelling, which reduces hydrocarbon production; this does not happen using when using $CO_2$.[36, 37] Individually these processes could stimulate significantly increased production, and in combination, they have the potential to transform the shale gas industry. These processes could have a significant impact over long term extraction that could increase cumulative gas production by 100% or more. Moreover, $CO_2$-based fracturing offers the potential for $CO_2$ sequestration [38, 39] both during the fracturing phase and after production has concluded.

Many of the theories and conclusions presented in this paper are founded on results obtained in an ongoing Los Alamos National Laboratory (LANL) research project that is examining the effectiveness of $CO_2$ as a fracturing fluid. The ultimate project goal is to make necessary measurements and develop models that can be used to compare different working fluids. Experiments across the pore, core and reservoir scales enable study of (1) fracture propagation in shale [28, 40, 41], (2) multi-phase fluid flow in fractures and the bulk rock matrix [42-44], and (3) how these mechanisms contribute to shale gas production [45]. This includes microfluidic experiments conducted under reservoir pressures and temperatures with geomaterials in order to characterize sweep efficiency and flow blocking. To characterize fracture propagation with fluids in layered shales, the project has developed a novel triaxial coreflood rig and has imaged microstructure-stress-fluid flow processes using tomography. Pore, core, and reservoir scale models have been developed from these experiments to study the hydrocarbon extraction processes shown in Figure 1. Through the combination of these methodologies, we have determined that non-aqueous approaches offer the potential to reduce the water footprint of shale oil and gas production and reduce environmental impacts, while also increasing hydrocarbon production.

# 2 Shale gas origins and production

The basic mechanisms for conventional shale gas production (i.e., water-based working fluids) are still poorly understood [45]. This lack of knowledge is one possible explanation for the relatively poor gas recovery rates of 20 to 30% [46]. It is assumed that natural gas and other hydrocarbons within shale formations are present as: (1) free gas in natural fractures that are either closed or open before hydraulic fracturing occurs, (2) free gas in the low permeability, low porosity shale matrix, and (3) gas adsorbed to kerogen in the shale matrix. Both (2) and (3) require microcracks that connect the low permeability matrix to the fractures in order for gas extraction to occur. Consequently, shale gas production entails liberating hydrocarbons from these locations and providing adequate gas transport mechanisms to the well bore; Figure 2 illustrates the production flow from gas-in-place locations, gas liberation mechanisms, and gas transport to the well bore and final production.

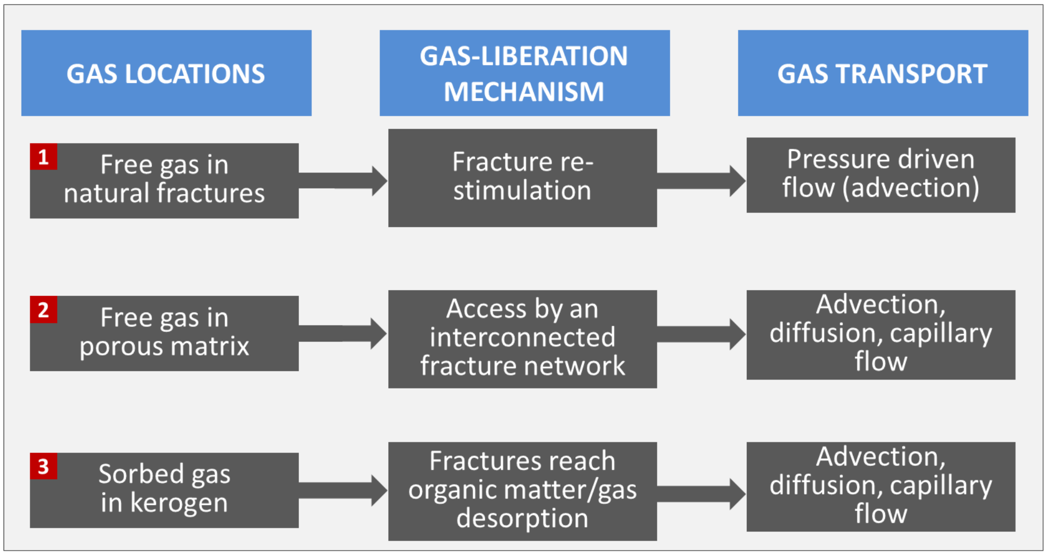
GAS LOCATIONS
GAS-LIBERATION MECHANISM
GAS TRANSPORT
1
Free gas in natural fractures
Fracture re-stimulation
Pressure driven flow (advection)
2
Free gas in porous matrix
Access by an interconnected fracture network
Advection, diffusion, capillary flow
3
Sorbed gas in kerogen
Fractures reach organic matter/gas desorption
Advection, diffusion, capillary flow

*Figure 2: Dominant gas-in-place origins, liberation mechanisms, and transport pathways. Gas present in re-stimulated natural fractures flows under the pressure gradient to the horizontal well. Free gas in the porous matrix accessed by the fractures and gas near (and adsorbed on) organic matter may be transported to the well by advection, diffusion, and/or capillary action.*

## 2.1 Shale gas production rates

Shale gas production curves typically follow an exponential decline in production over their first two years, followed by a long production tail that can last 20 years or more. Figure 3 shows this production decline for a representative well in the Haynesville formation in Texas. Although the fundamental science and mechanisms driving this decline are poorly understood and quantified, we can use modeling approaches to imitate production at a typical well site and understand the physical reasons for the observed decline. To evaluate the contribution of fundamental mechanisms to shale gas production, we have performed simulations using a novel reservoir-scale discrete fracture network (DFN) modeling approach [45] , in which reservoir fractures are modeled as a set of two-dimensional planes in three-dimensional space with specified shape, orientation, aperture, and permeability. Figure 4 shows a network of 376 natural fractures based on a shale site in the Upper Pottsville formation in Alabama [47], generated using the feature rejection algorithm for meshing introduced by Hyman et al. [48]. Six additional fractures are introduced perpendicular to a horizontal well that runs through the center of the domain to imitate hydraulically generated fractures. These man-made fractures intersect the network of natural fractures and provide additional pathways for hydrocarbons to reach the production well. The horizontal well is located in the center of the domain as shown in Figure 4. Apertures of the natural fractures are proportional to their radius with minimum, maximum and average apertures of 0.224 mm, 0.413 mm, 0.264 mm, respectively. For all the hydraulic fractures, an aperture of 3.53 mm was chosen. The corresponding permeabilities were evaluated using the "cubic-law" approximation [49]. Additionally, a porosity of 0.2 was set in the fractures. In the simulation, the pressure in the well is set at 17 MPa (equivalent to approximately 2 km in depth), and pressure at the boundaries parallel to the well are set at 21 MPa; the subsurface flow simulator PFLOTRAN [50], a massively parallel code, is used to obtain the pressure solution in the network shown Figure 4. Particles representing gas packets are uniformly distributed throughout the network, and their travel time to the well is computed using techniques introduced by Makedonska et al. [51]. A selection of the particle trajectories is shown in the right subfigure of Figure 4. Physically, these particle exit times represent the initial fracture drainage out of the network; no additional physical mechanisms, such as matrix diffusivity, are included.

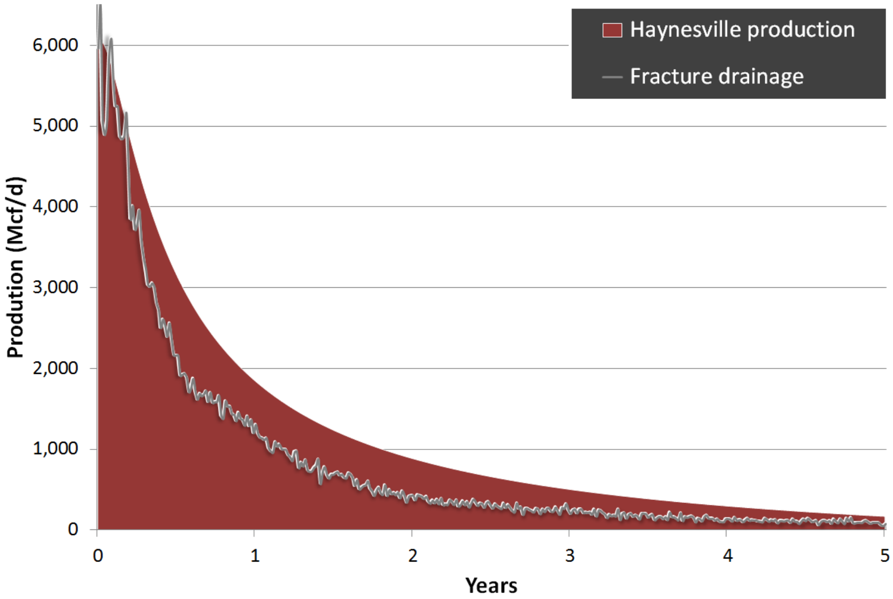

*Figure 3: Shale gas production for the Haynesville, TX, formation (red area) and simulated production from large fracture drainage (grey line). Haynesville production is modeled from Middleton et al. [52]*

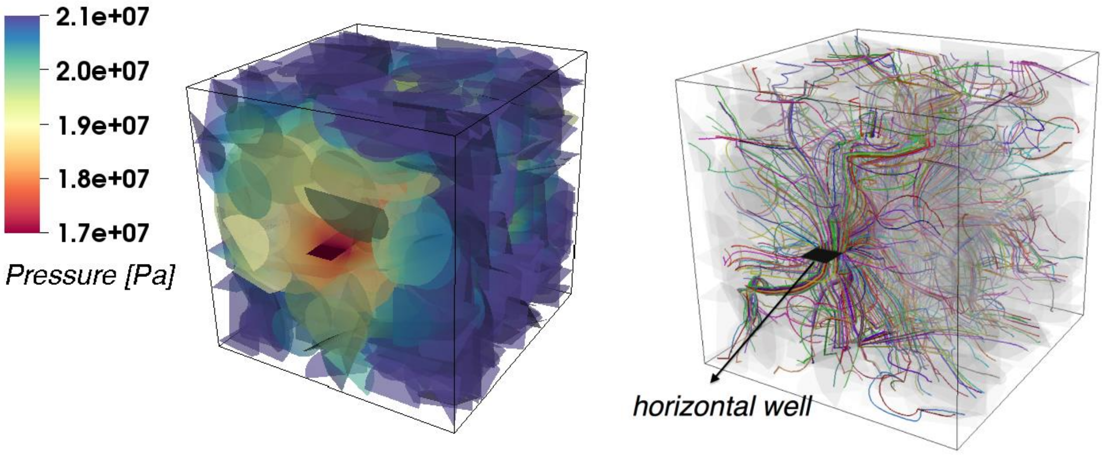

*Figure 4: Results from a reservoir-scale modeling approach to obtain production curves through fracture drainage. LEFT: Pressure solution in the discrete fracture network. RIGHT: Pathways of gas packets from the reservoir to the horizontal well. A network of 376 natural fractures based on data from upper Pottsville formation is generated in a domain of size 200 x 200 x 200 m. A horizontal well is placed in the center of the domain and six equally spaced fractures perpendicular to the horizontal well are created to represent hydraulically generated fractures. A pressure of 21 MPa is applied to the boundaries parallel to the horizontal well while a pressure of 17 MPa is maintained at the well. 100,000 particles were tracked during the simulation, though only 1,000 pathways are shown for visualization purposes. The pressure gradient between the boundaries and the well draws the gas packets towards the well.*

The grey line in Figure 3 is generated using 100 000 particle exit times, and the maximum of the virtual production curve is matched to the peak production of a typical Haynesville well. This virtual curve matches the Haynesville gas production well for the first year, and indicates that this initial fracture flush from large fractures represented by the DFN is the likely dominant production mechanism during the first year. After the first year, the curve generated using the DFN simulation is lower than the field data, indicating that fracture drainage begins to explain less of the production (we have considered only advective flow of free gas in the fractures in the simulation) and other mechanisms, such drainage of gas by matrix diffusion and desorption, begin to dominate production (which are not included in this model).

Our hypothesis, and others, is that long-term production is controlled by smaller scale phenomena [40]. Specifically, that cumulative production over decades is controlled by how well hydraulic fracturing increases the shale's permeability and ease the transport of gas to the large fracture network and then to the well. If a non-aqueous fluid, such as $CO_2$, can perform better than water as a fracturing fluid, then the long-term cumulative production will increase. Figure 5 shows three hypothetical production curves based on enhancing specific gas migration mechanisms over the Haynesville production curve. These curves are not based on actual model runs (such models do not currently exist) and are meant to broadly illustrate the potential impact of using non-aqueous fracturing fluids. The impact of these enhancements to the daily production curves is shown by the cumulative production curves displayed in Figure 6. Together, these figures illustrate several hypothesized scenarios based on best estimates from ongoing experiments and modeling. Note that even a moderate increase in the gas production rate due to $CO_2$-enhanced fracturing translates into a major increase in cumulative production. Similar conclusions can be drawn for both reduced flow blocking and desorption, all of which are expected outcomes of using $CO_2$ as a working fluid. Details of these processes are discussed in the following sections. Individually these processes can stimulate significantly increased production, and in combination, they have the potential to transform the shale gas industry. For example, if enhanced fracturing exposes 50% more shale surface area then desorption and reduced flow-blocking processes generated by $CO_2$ will have a much greater volume of shale to work with. Further, these processes are likely to make a significant impact over time that could significantly increase cumulative gas production. In this case (Figure 5 and Figure 6), enhanced production processes are adding approximately 80% to cumulative production over a five-year period; ultimately, this increase could be much higher. In the next section, we use a combination of new experimental and modeling data to demonstrate and theorize how $CO_2$ could significantly increase shale gas production.

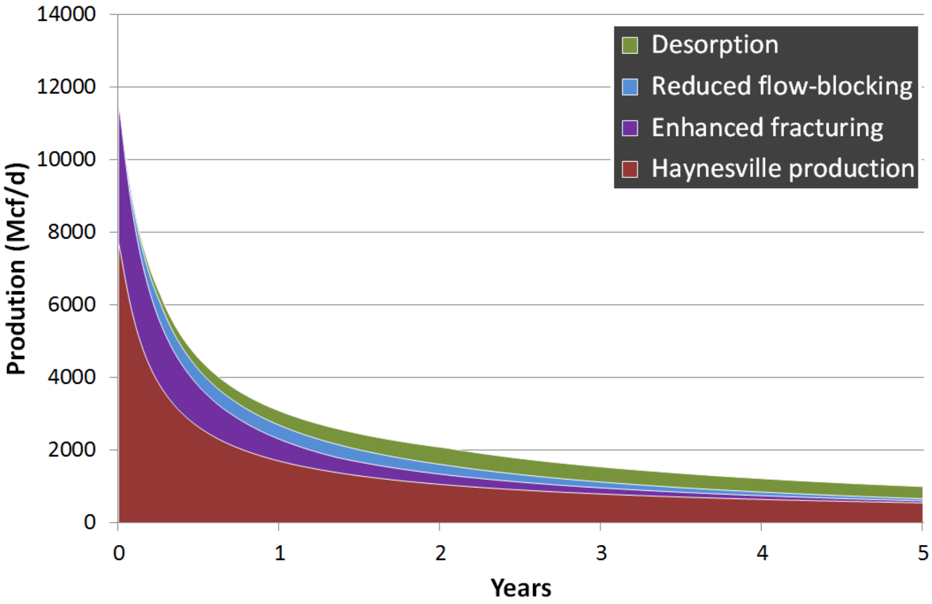

*Figure 5: Hypothesized enhanced shale gas production rates using a $CO_2$ working fluid. Here, we estimate that enhanced fracturing (purple area) could initially increase production by as much as 50%, compared with a conventional water fracturing fluid (red area). The enhanced fracturing effect drops over time, in this case to around 10% after 10 years. Reduced flow blocking (blue area) increases production around 10-20%. Having a compound effect on top of enhanced fracturing. Finally, after 1-2 years, we hypothesize that desorption (green area) could increase production by as much as 50%, though this effect is most prominent in the tail.*

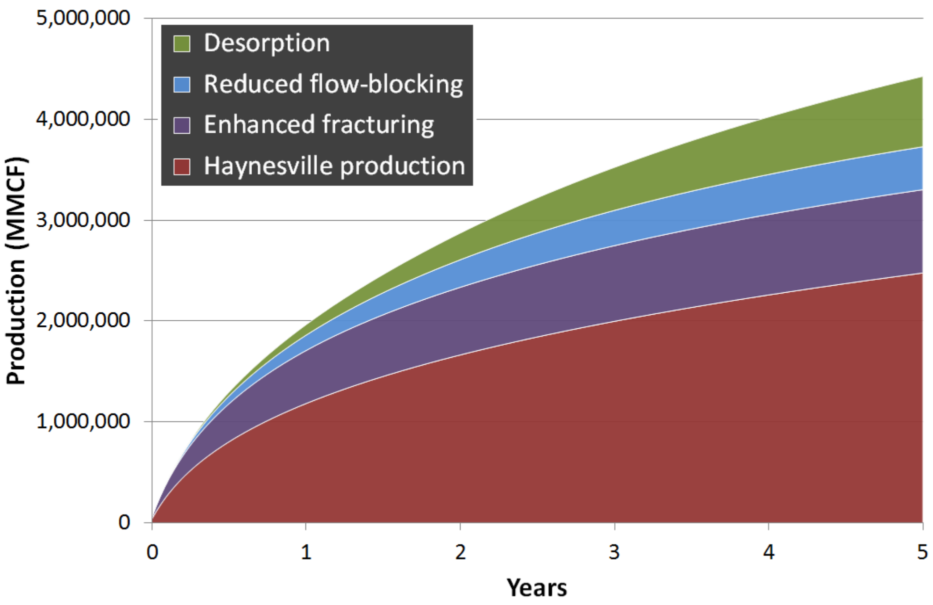

*Figure 6: Cumulative hypothesized production as a result of $CO_2$-based enhanced production. The chart demonstrates that a small impact in the tails of production rate (see Figure 5) can have a large impact on cumulative production.*

## 3 $CO_2$: Ramifications of an Alternative Working Fluid

Lack of water in some regions, the need for flow-back water disposal wells, and a growing belief that more stringent fracturing regulations are pending has generated significant interest in using $CO_2$ as a working fluid in hydraulic fracturing. $CO_2$ has been used previously as a fracturing fluid with encouraging results. In a DOE-sponsored experiment conducted before the hydraulic fracturing boom, the use of $CO_2$ resulted in up to five times more gas production compared to aqueous fluids, required no additives, and greatly minimized water usage; however, the test did not produce consistently positive results [30, 53, 54]. A more recent report states that $CO_2$-based fluids provide an interesting, although as yet unproven, possibility for enhancing gas recovery, reducing water required, and sequestering $CO_2$ [55]. Under *in situ* reservoir conditions $CO_2$ is a supercritical fluid (critical temperature $31^oC$; critical pressure 7.4 MPa) and exhibits favorable miscibility with hydrocarbons, making it beneficial for EOR [56].

In this section, focus is placed on the production effect of using $CO_2$ as a working fluid. We begin with phenomenon on the meter scale and move down to the nanometer scale. Through experimentation and a review of existing literature, we have compared the important basic aspects of $CO_2$ and water. We argue that $CO_2$ should dramatically increase production while lowering environmental impacts through a variety of physical mechanisms including: (1) additional fracture propagation due to isenthalpic expansion, (2) hydrocarbon miscibility with $CO_2$ should minimize flow blocking in small pores, and (3) the potential exchange of $CO_2$ with methane adsorbed in organic-rich regions of the shale (i.e., desorption). Finally, $CO_2$-based fracturing offers the potential for $CO_2$ sequestration both during the fracturing phase (predominantly due to $CO_2$ preferentially displacing adsorbed methane [35]) and after production has concluded via injection into the depleted reservoir.

## 3.1 Enhanced fracturing

Effective hydraulic fracturing requires the creation of fracture networks that can drain the matrix of hydrocarbons. Fracturing formation is affected by the local stress field and the rock properties, however, the fluid properties also affect the types of fractures that are created. We hypothesize that supercritical $CO_2$ is able to generate more extensive and complex fracture networks than water-based working fluids; water tends to produce more planar fractures with less surface area. Specifically, we believe two distinct mechanisms lead to $CO_2$-enhanced fracturing: low viscosity and thermo-mechanical effects.

Slickwater is widely used in the shale gas industry and is believed to produce more complex fractures than “normal” water [57-59]. Slickwater is a low-viscosity water that is able to generate narrow fractures and more complex, multi-orthogonal fracture networks [57]. This enhanced fracturing is principally due to the lower viscosity of the water. Slickwater additives are largely composed of a friction reducer, along with other additives including biocides, scale inhibitors, and surfactants [60]. After fracturing, the low viscosity slickwater is removed and "normal" water is often introduced to carry proppants. We hypothesize that $CO_2$ would create even more complex and extensive fracture networks than slickwater due to its substantially lower viscosity than even the best slickwaters. In addition, we believe that supercritical $CO_2$ would require fewer additives, such as biocides and surfactants, while still remaining an increasingly effective fracturing fluid. Note that the viscosity of $CO_2$ can be increased substantially by addition of $CO_2$-philic species, including formation of gels [61-63], though the costs and environmental impact might be prohibitive. Following fracturing, viscosity-modified $CO_2$ can be employed to deliver proppants as needed.

We also believe that supercritical $CO_2$ will have significant thermo-mechanical effects that will enhance fracturing. At the moment fractures are formed, they instantaneously create void space into which the fracturing fluid flows. While filling of newly created voids with fluid is expected to take place over relatively small time-scales, important differences in dynamic behavior may occur depending on whether the fracturing fluid is water or $CO_2$. The differences originate from the thermo-physical properties of the two fluids. Of particular interest is the temperature change resulting from an initially isenthalpic expansion (i.e. a Joule-Thompson throttling process [64]) into the void space created by a fracture. As a preliminary calculation, we employed the commonly used Peng-Robinson equation of state to estimate temperature changes upon isenthalpic expansion of both pure water and pure $CO_2$ from reservoir conditions, taken to be 20.69 MPa and 50 °C, into a void space. Virtually no change in temperature was seen in water upon expansion down to pressures as low as 0.689 MPa. However, $CO_2$ cooled roughly 200 °C and partially liquefied when subjected to the same isenthalpic reduction in pressure. During this expansion, a thermal shock (stress) at the crack tip could form promoting additional fracture propagation. Of course, the fracturing pressure will ultimately be re-established within this newly created fracture. However, during the transient low-pressure period, the reduced temperatures could increase crack propagation provided heat is transferred rapidly from the crack tip to the cool fluid.

## 3.2 Fluid transport in fractures and matrix pores

Once in the connected fractures, hydrocarbons must migrate through the network to the producing well. At the nano- and meso-scales, surface tension often dominates fluid transport dynamics for hydrocarbon-brine systems. We have identified several key issues to investigate in the laboratory and through computational simulations including: (a) wettability and the viscosity difference between shale and the working fluid will govern the penetration of the working fluid into complex branching fracture networks (e.g. Figure 7 highlights a relatively simple fracture pattern), (b) because aqueous systems are immiscible with hydrocarbons, fracture networks may become blocked by residual water trapped at pinch-points within the fracture ($CO_2$, because it is miscible, may allow unrestricted migration of hydrocarbons), (c) dead-end pores may trap hydrocarbon in aqueous systems while $CO_2$ could dissolve into and liberate trapped hydrocarbon, and (d) some components of natural gas, a complex multicomponent hydrocarbon, can condense as liquid due to pressure gradients at material interfaces causing additional flow blockage that can be relieved by miscibility with supercritical $CO_2$.

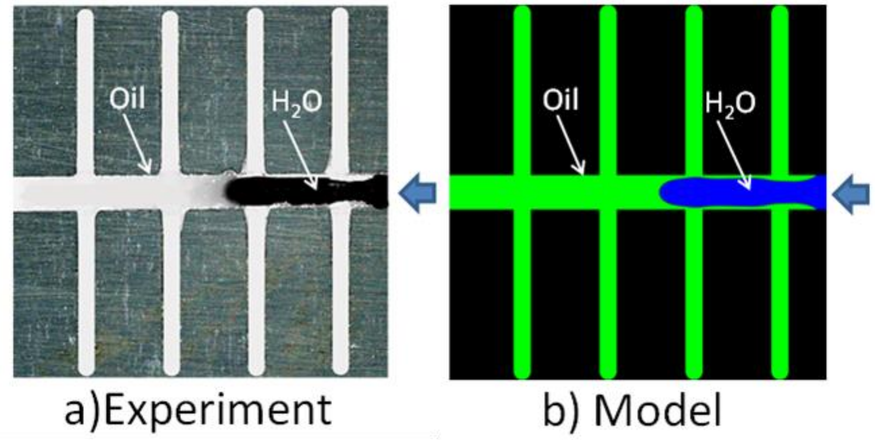

*Figure 7: Displacement of hydrocarbon by water in a shale wafer. Left: Microfluidics experiment, Right: Lattice Boltzmann Simulation. Immiscibility of oil and water effectively traps the oil in the micropores. The main channel is approximately 0.5 mm in width.*

These issues are being examined using a combination of ambient- and high-pressure microfluidics experiments and lattice Boltzmann model (LBM) simulations. By using actual shale samples, the penetration of water (and eventually $CO_2$) can be observed under *in situ* shale gas conditions. Lattice Boltzmann models are appropriate tools in simulating these processes since they capture intra-pore geometries, complex flows, and all relevant physicochemical processes. Our LBMs can resolve multiphase flow [42-44, 65-68], multi-component chemistry [69-78], and phase transitions [79]. Figure 7 (a) shows a microfluidic experiment in which a simple fishbone fracture pattern has been etched into Marcellus shale sample. The experiment was performed at 20 °C and 1 atmosphere (approximately 1 MPa), a surface tension of 0 .0427 N/m, and a flow rate of 1 ml/hr. The dynamic viscosities of the silica oil and water were 4.6 and 1 centipoise respectively. Figure 7 (b) shows a LBM simulation of the experiment that captures the fingering as the invading immiscible water displaces hydrocarbon, but bypasses the hydrocarbon in dead end fractures resulting in poor sweep. The simulation was performed using the open source code Taxila LBM [42]. A grid of 1104×872 is used, with a resolution of 10 microns/grid cell. Flux is specified at the entrance and pressure prescribed at the exit. At first glance, this initial two-phase flow example may appear overly simplistic; the variability of complex three dimensional pore spaces induces highly heterogeneous flow fields [80, 81]. However, in this flow geometry the finger width is controlled by flow rate and the fluid viscosity ratios, and the network topology also affects the finger width due to the interaction between the side channel and the primary; the LBM simulation correctly captures this interaction.

Real rock micro-model experiments at geologically relevant pressures and temperatures are exceptionally difficult to perform; the experiment demonstrated in Figure 7, for example, was performed in ambient conditions. Consequently, few, if any, such experiments currently exist for injecting $CO_2$ into real rock under such conditions. However, geologically-realistic experiments are absolutely essential to characterize sweep efficiency since key properties, such as surface tension, viscosity, and miscibility, are pressure and temperature dependent. Moreover, fracture flow is directly affected by the rock matrix properties; this cannot be replicated in engineered (e.g., glass, silicon) micro-models. Figure 8 shows results from a first-of-a-kind microfluidic experiment where supercritical $CO_2$ ($scCO_2$) was injected at constant flow rate (0.1 ml/min) from left to right into a (dyed) water-saturated fracture under representative reservoir conditions (8.62 MPa and 50 °C). The fracture pattern, modeled from an actual fracture, was laser etched into a Utica shale sample. The fracture roughness has a significant impact on interfaces separating fluids, resulting in localized supercritical $CO_2$ flow paths within the fracture. In addition, imbibition of water into the shale micro-model and dissolution of supercritical $CO_2$ bubbles into water was observed in the experiment. These experiments allow a complete visualization/characterization of the key role that $scCO_2$ plays unlocking the system (see next section); at supercritical conditions, $scCO_2$it is miscible with the most common liquids present in the reservoirs including water and hydrocarbons. Further research at reservoir conditions will include the sweep efficiency experiments using supercritical $CO_2$ and water in complex fracture networks. These experiments will address three-phase system flow involving resident fluids such as brine and hydrocarbons (e.g., oil, gas).

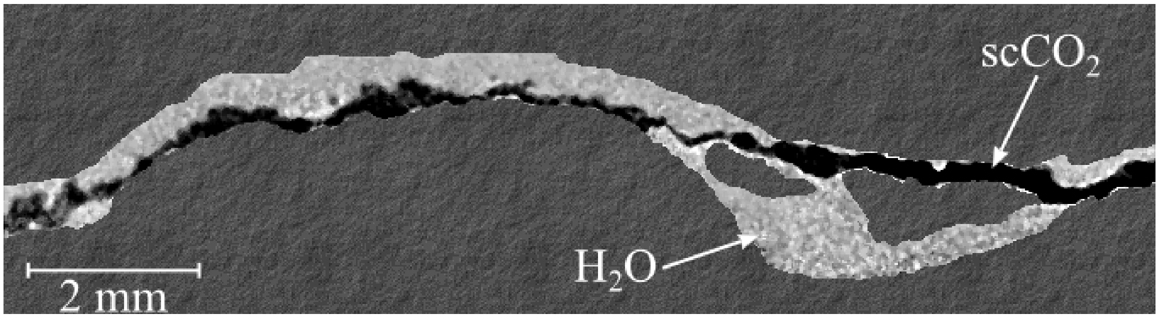

*Figure 8: Etched shale micro-model experiment at high pressure and temperature (8.62 MPa and 50 °C) with the displacement of water (white) by supercritical $CO_2$ (black). Injection from left to right at constant flow rate (0.1 ml/min).*

## 3.3 Flow blocking

Surface tension estimates suggest that water imbibed into pores during fracturing can effectively block pore throats and trap liquid hydrocarbon; this pore-blocking phenomenon would not occur using miscible supercritical $CO_2$, highlighting an important potential advantage. Nanometer-sized pores account for a substantial fraction of the porosity in a typical shale [82-84], and at such scales, surface tension (capillary effects) dominates fluid transport.

To provide some insight into the importance of surface tension, consider the following situation. Assume that a straight cylindrical pore throat connects a water-filled induced fracture to a larger liquid-hydrocarbon reservoir, and that the interconnecting pore throat is filled with liquid hydrocarbon at the onset of fracturing. During fracturing, the water pressure must exceed the reservoir pressure, which pushes water from the induced fracture some distance into the pore. For our example, the pressure difference between the water and the reservoir may be ~10 MPa during fracturing. Later, during the gas production phase, the injected water pressure is reduced and water is (partially) removed as flow-back water. At this point, the induced fracture is assumed to be predominately filled with desorbed methane. Furthermore, during the production phase the pressure in the pore and hydrocarbon reservoir now exceeds that found in the induced fracture. If one assumes that $\Delta P$ is now, say, ~5 MPa, but in a direction opposite to what existed during fracturing, one might expect that hydrocarbons in the reservoir would flow through the pore and into the induced fracture network. However, at the mouth of the pore throat (which is in contact with the induced, methane-filled, fracture) the interfacial tension is between water and methane. At the other end of the water slug (within the pore throat) the interfacial tension is between water and liquid hydrocarbon. The two interfacial tensions and contact angles differ, with the water-liquid hydrocarbon interfacial tension being higher [85]. If the pore diameter is small enough, the difference in interfacial tensions can lead to forces that balance the production phase pressure gradient. At that point, the water slug is not driven out and the remaining water effectively "blocks" the pore. That is, the pressure difference during production may not be enough to overcome the surface tension forces holding water within nanometer scale pores. Laboratory analysis of shale samples obtained from the field has shown that a substantial fraction of the naturally existing matrix porosity consists of pores with characteristic diameters in the nanometer to tens-of-nanometer range [82-84]. Now consider a miscible $CO_2$ phase with liquid hydrocarbon. The pore throat and the hydrocarbon pore body are now a single phase and most only overcome the surface tension at the mouth of the pore-throat leading into the induced fracture.

## 3.4 Adsorbed gas

The overall quantity of methane present in shale, together with its low porosity, suggests that much of the methane gas contained must be adsorbed under *in situ* reservoir conditions. The appreciable electrostatic (quadrupole) moment present in the $CO_2$ molecule suggests that it may result in stronger interactions with organic constituents when compared to a non-polar molecule such as methane. Hence it may preferentially adsorb. We performed an initial assessment of the impact of preferential sorption using recently reported $CO_2$ and $CH_4$ adsorption data [86-89] in shale that shows a clear propensity for $CO_2$ to adsorb onto shale relative to methane. In Figure 9, Langmuir adsorption parameters deduced from the cited single gas adsorption measurements were used in a multi-component extension of the Langmuir adsorption isotherm [90]. The results from this calculation suggest that displacement of adsorbed methane by $CO_2$ is likely to occur under fracturing conditions. While these initial calculations are encouraging, refinements are clearly required to provide quantitatively accurate assessments. For example, the Langmuir model assumes the heat of adsorption is identical for each surface adsorption site, there are no interactions between the adsorbed species, and ignores non-idealities in the fluid phase. Also, $CO_2$ sorption is expected to depend strongly on both shale chemistry and water content, which calls for additional experimental work.

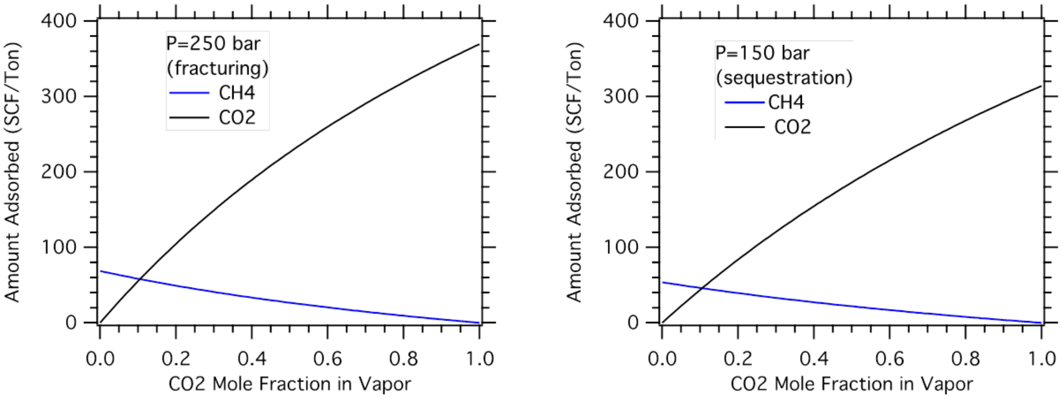

*Figure 9: Equilibrium distribution of $CO_2$ and $CH_4$ adsorbed in shale using reported Langmuir adsorption parameters [86-89]. Following the cited sources, quantities are given in standard cubic feet (SCF) per short ton. Under assumed fracturing conditions of 250 bar (left; 25 MPa), $CO_2$ adsorption is increasingly favored at higher vapor mole fractions, which should promote $CH_4$ desorption and higher net production. Assuming a post-production overpressure of 150 bar (right, 15 MPa), enables one to estimate the amount of $CO_2$ adsorbed and hence the sequestration potential of the formation.*

## 3.5 $CO_2$ sequestration

Following the production phase, if one assumes the shale formation is ultimately pressurized with $CO_2$ to 15 MPa, the adsorption calculations reported in Figure 9 suggest that as much as 9.43 cubic meters of $CO_2$ could be adsorbed per metric ton of shale. Thus, a fully accessible shale seam 1000m by 300m by 20m could potentially adsorb and sequester up to $4.8 \times 10^5$ cubic meters of $CO_2$. Thus, $CO_2$-based fracturing may offer significant potential for $CO_2$ sequestration during the fracturing phase. After production has concluded, additional $CO_2$ sequestration could be achieved by treating the fractured shale as a storage reservoir. There is a particularly large $CO_2$ mitigation potential when hydraulic fracturing is coupled with anthropogenic $CO_2$ sources [91]. Tao and Clarens [92] estimate that, for post-production shale gas, "the Marcellus shale alone could store between 10.4 and 18.4 Gt of $CO_2$ between now and 2030, which represents more than 50% of total U.S. $CO_2$ emissions from stationary sources over the same period". Consequently, if future $CO_2$ emissions are actively managed, shale gas production and subsequent depleted gas fields could provide substantial $CO_2$ storage capacity. However, such initial projections may be somewhat optimistic since imperfect connectivity between induced and existing fractures will result in regions of the formation that are effectively inaccessible for sequestration purposes.

Use of $CO_2$ for shale gas production also involves an interesting comparison with $CO_2$ used for EOR. For shale gas, increased use of $CO_2$, on a well-by-well basis, would likely be associated with increased hydrocarbon production due to preferential displaced of sorbed methane. That is, a shale gas operator is happy to "lose" as much $CO_2$ as possible. For EOR, increased "loss" (or storage) of $CO_2$ is not necessarily associated with increased oil production and thus the operator would try balance $CO_2$ injection and oil production. $CO_2CO_2CO_2CO_2$Hydraulic fracturing in order to enhance permeability has been shown to increase injectivity in saline aquifers, but it also reduces long-term trapping of carbon dioxide [93]. Quantifying this relationship in tight shale formations is the focus of current research.

# 4 Remarks

The extraction of oil and gas from shale formations is enhanced by the process of hydraulic fracturing, which increases the permeability of the formation and thereby eases gas transport. Currently, water with additives is the primary fluid used in commercial shale gas and oil production due to its low cost, ready availability, and its suitability for fracturing. However, the long-term use of water in hydraulic fracturing is under evaluation by industry. The most notable concerns include: (1) water-availability issues related to drought that have impacted fracturing, including the denial of drilling permits, (2) treatment and/or disposal of contaminated flow-back water is costly, (3) induced seismicity that results in low-level earthquakes has been linked to deep reinjection of flow-back water, and (4) the possibility of potential freshwater contamination during the injection/production phases as well as with water disposal. These concerns have stimulated exploration into the use of non-aqueous fracturing fluids including supercritical $CO_2$.

Through novel, albeit preliminary, experimentation, heuristic reasoning, and a review of the current literature, we argue that supercritical $CO_2$ might be a feasible alternative to water as a working fluid. Although we have focused on shale gas production many, if not all, of our work is equally applicable to shale oil production. The use of $CO_2$ should increase production while lowering environmental impacts through a variety of physical mechanisms including: (1) additional fracture propagation, (2) reduced flow blocking, and (3) desorption. Moreover $CO_2$-based fracturing offers the potential for $CO_2$ sequestration both during the fracturing phase and after production has concluded, predominantly due to $CO_2$ preferentially displacing adsorbed methane.

Potential drawbacks include the increased expense of capturing-pressurizing-transporting $CO_2$, robust accounting of $CO_2$ emissions and storage, pressure safety at the site, separation of hydrocarbons and brine from the flow-back $CO_2$, and re-pressurization of flow-back $CO_2$. In a few cases, the fracturing operation may have access to existing $CO_2$ pipelines, which typically involve supercritical pressures or are co-located at sites where $CO_2$ is a waste steam. However, in most cases expenses will be incurred to transport $CO_2$ to the drilling site. Upon completion of the fracturing phase, the $CO_2$ is removed to initiate the production phase. It is expected that during this period a mixture of $CO_2$ and natural gas will be produced. Either the gases must be separated in order to meet pipeline and market specifications for natural gas, which involves an additional expense [94], or the natural gas produced during the flow back period is simply considered "lost." Reuse or sequestration of the $CO_2$ following the well's production phase will almost certainly involve re-compression expenses. In addition, there are some characteristics of $CO_2$ under reservoir conditions that may be of concern. In addition to concerns over the proppant-carrying capacity of supercritical $CO_2$, water present in the formation will tend to dissolve in the supercritical $CO_2$. If water is removed from concentrated brines as part of equilibration with the supercritical $CO_2$, then it is possible that the remaining brine becomes supersaturated with dissolved salts and precipitation occurs. Precipitation of mineral salts could contribute to the blocking of small pores containing water and hydrocarbon, which could undesirably restrict subsequent removal (flow) of the hydrocarbons.

There are several factors that impact drilling and production costs such as formation properties, fracturing water composition (additives), fracturing fluid disposal, drilling parameters, and their associated costs. The overall economic comparison between water and $CO_2$ (or any alternative working fluid) depends primarily on its influence on gas production effectiveness as well as additional costs associated with environmental impacts, the economics of $CO_2$ delivery, and flow-back $CO_2$ treatment cost. It is likely that industry will only switch to non-aqueous working fluids if there is a demonstrable and reliable increase in production that justifies the increased costs of alternative fracturing methods. The final economics of $CO_2$-promoted shale gas will depend on the source of $CO_2$; for instance, price of purchased $CO_2$ varies widely between sources such as bio-refineries, ethylene, extracted $CO_2$, and coal-fired and natural gas power plants [94].

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